

PAPER • OPEN ACCESS

Hydrometallurgical Technology for Processing of Galvanic Sludges

To cite this article: O Yu Makoskaya *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **969** 012055

View the [article online](#) for updates and enhancements.



The Electrochemical Society
Advancing solid state & electrochemical science & technology
2021 Virtual Education

Fundamentals of Electrochemistry:
Basic Theory and Kinetic Methods
Instructed by: **Dr. James Noël**
Sun, Sept 19 & Mon, Sept 20 at 12h–15h ET

Register early and save!



Hydrometallurgical Technology for Processing of Galvanic Sludges

O Yu Makoskaya, K S Kostromin and N I Bryantseva

Institute of New Materials and Technologies, Ural Federal University named after the first President of Russia B. N. Yeltsin, 19, Mira Street, Ekaterinburg, 620002, Russia

E-mail: o.i.makovskaia@urfu.ru

Abstract. The problem of processing galvanic sludges, formed as a result of neutralization of technological solutions and wastewater containing heavy non-ferrous metals is considered. At present, sludges are transported to disposal area and are not used in any way. Typically, such sludges contain significant amounts of chromium and nickel, which creates environmental hazard. Investigated sludge contains up to 6.6% Ni and up to 7.4% Cr. The hydrometallurgical technology for processing of these sludges has been developed. Solutions of sulfuric acid and ammonia were used as lixiviants. It is shown that when using a solution of sulfuric acid with pH=1.5, extraction of up to 93.3% Cu, 70.2 Ni, 90.3 Zn is achieved. For selective recovery of nickel from leachates the process of sorption concentration by Lewatit TP207 is proposed.

1. Introduction

Galvanic workshops produce large amounts of waste waters. Solid waste, called galvanic sludge is formed as result of the physicochemical treatment of that waste water. Galvanic sludge is considered to be one of the most highly toxic types of waste and stored mainly in sludge pits. Such practice has not any economic or environmental advantages [1, 2].

In order to reduce the environmental hazard of galvanic production wastes deposited in the sludge, methods of chemical fixation by means of ferritization of solid phase of wastes, silicification, solidification of wastes with the use of inorganic and organic binders, as well as sintering are used [3–7]. One of the ways of processing of galvanic sludges is their application as filling agents and plasticizers in concretes, asphalt concretes and building mortars [8–10]. It is possible to obtain pigments from sludge components [11]. The work [12] describes production of nickel hydroxide suitable for use as an active component of cathode mass for manufacture of Ni(OH)₂ electrode of a nickel-cadmium (iron) battery.

At the same time, the sludge can be considered as a significant source of heavy non-ferrous metals and chromium. Content of copper, chromium, nickel or zinc can reach 30 % of dry weight. Development of alternative and effective ways reducing the impact on the environment and providing extraction of valuable metals contained in these sludges are of paramount importance.

Considerable variations in sludge composition create additional difficulties for the development of a comprehensive sludge treatment scheme. The most expedient way to process such complex raw material is hydrometallurgical, providing selective extraction of non-ferrous metals.

Mineral acids, ammonia, chelators are used as a solvent. There is information about the use of NaOH as a solvent [13]. In [14] a combined method of recycling of galvanic sludges was proposed, which



includes galvanic sludge mixing with additives containing chlorine ions in the ratio $\text{Cl}^- : \text{Me}^{n+} = 1.1:1$, mechanochemical activation of mixture obtained by dry grinding in the ball mill to a size of 0.5-5 microns, subsequent heat treatment in a muffle furnace at the temperature of 450-500 °C, the resulting cake leaching by waste water own galvanic production at pH = 3.

Further processing of the obtained solutions is also possible by several methods. The most widely used liquid extraction [15, 16] and ion exchange [17]. These methods make it possible to selectively isolate valuable components from solution.

In any case, the choice of processing technology is carried out after studying the chemical and phase composition of each individual sludge sample.

2. Experimental

Sludge produced by nickel-plating/chrome-plating units has been studied. Sludge samples were taken from different points of the sludge storage facility and have noticeable variations in the composition (table 1), so the samples taken for the study were averaged. The phase composition of the sludge is represented by the following compounds: $\text{Ni}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, Ca_2SiO_4 , SiO_2 , $\text{Cr}(\text{OH})_3$. The sludge is mixed with sand due to the conditions of its placement in the sludge storage.

Table 1. Chemical composition of sludge.

Sample	Content (%)						
	Ni	Zn	Cu	Pb	Fe	Ca	Cr
1	3.97	1.26	0.82	0.035	0.58	0.01	4.71
2	6.98	1.43	1.14	0.11	0.64	1.71	8.02
3	3.88	1.73	1.03	0.25	0.81	0.84	2.11
4	3.46	1.65	0.93	0.21	0.74	2.19	1.81
5	7.06	1.94	1.55	0.23	0.98	1.21	7.11
Average sample	6.64	1.33	1.06	0.13	0.58	1.26	7.41

Ammonia leaching of the initial sludge was carried out at pH 8–9, temperature 25 °C, sludge mass 20 g, the volume of the solution 150 cm³, the duration of the process 1.5 hours. The results of the experiment are shown in figure 1.

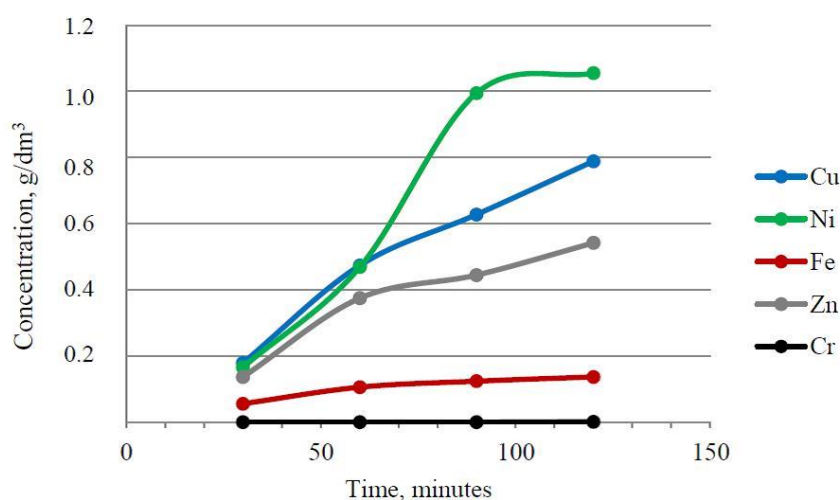


Figure 1. Kinetic of sludge leaching by NH_4OH .

As a result of ammonia leaching within 90 minutes, solutions containing about 1 g/dm³ of nickel and 0.628 g/dm³ of copper were obtained. The rate of nickel transfer to the solution reduces at further leaching. The advantage of ammonia leaching is minimal transition of iron to solution and complete absence of chromium in leachate. However, recovery of nickel in the solution does not exceed 50 % of its initial content in the sludge.

Sulphuric acid has proved to be one of the best reagents from previously tested solvents [18, 19]. Therefore, subsequent leaching experiments were carried out using sulfuric acid.

Sulphuric acid leaching of the initial sludge was carried out at pH 1.5; temperature 25 °C, sludge mass 10 g, solution volume 100 cm³, pH was regulated by the droplet adding of H₂SO₄ (1 M). Dependence of metals concentration in solution and extent of metals extraction in solution from duration of leaching is presented in figure 2.

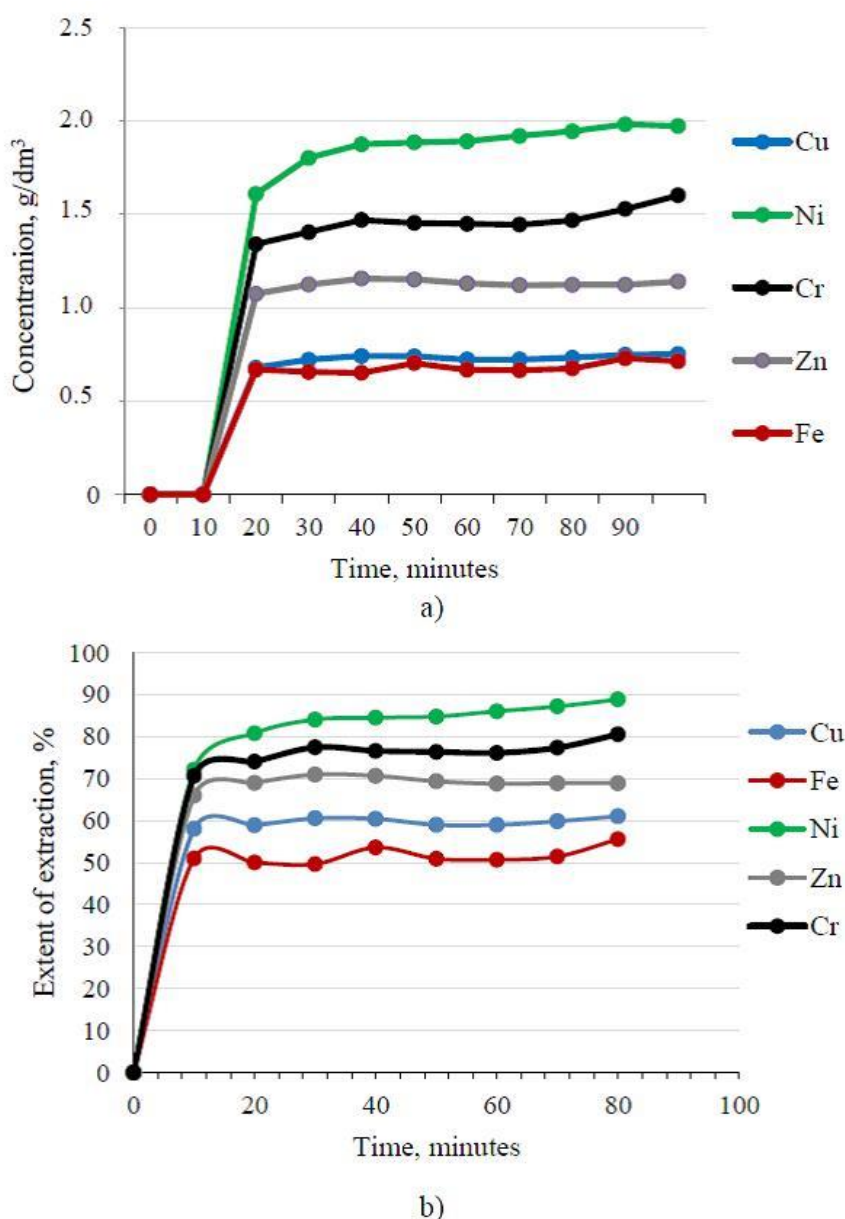


Figure 2. Dependence of metals concentration in solution (a) and extent of metals extraction in solution (b) from duration of leaching.

Nickel recovery reaches 90 % at leaching by solution of sulfuric acid during 90 minutes. The main disadvantage of sulfuric acid leaching is the lack of selectivity. Up to 80 % of chromium and up to 50 % of the iron contained in the sludge passes into the solution. It is necessary to solve the problem of separation of these elements at further processing of solutions.

Sorption on ion exchange resins was used to extract nickel from sulphuric acid leaching solutions. It is advisable to use a sorbent that preferably absorbs nickel at its joint presence with chromium in the solution. Based on published data, the following sorbents were selected for the tests: KU-2×8, Lewatit TP207, Purolite C104, Purolite S930.

To determine the static exchange capacity, all the ion exchangers were converted to the H^+ -form by washing with 1N H_2SO_4 . A sample of ion exchanger (0.5 g) was brought into contact with 50 cm³ of nickel (II) solution (1 g/dm³). To determine the capacity for chromium (III), a solution with concentration of 0.63 g/dm³ was used. A static exchange capacity was calculated for each ion exchanger; the results are shown in table 2.

Table 2. Ionites static exchange capacity for nickel and chromium.

Ionite	SEC for Ni(II) (g/g)	SEC for Cr(III) (g/g)
Purolite S930	0.039245	0.0002
Lewatit TP-207	0.040525	0.0001
KU 2×8	0.043695	0.0266
Purolite C104	0.03046	0.0077

Based on the obtained data, Lewatit TP-207 was selected as having the best indices for metal selection. Ionite Lewatit TP-207 is a weakly basic macroporous cation exchange resin with chelate groups of iminodiacetic acid. Ionite is intended for the selective removal of heavy non-ferrous metal ions from weakly acidic and slightly alkaline solutions. This ion exchanger showed a high sorption capacity with respect to nickel, but insignificant sorption of chromium when they collectively presence in solution.

The effectiveness of the sorption process strongly depends on the pH value; therefore, an experiment to study the effect of pH on the nickel sorption process was conducted. At pH=2, the concentration of H^+ ions in the functional groups is high and pushes metal cations into the solution due to the high degree of protonation of the functional groups, i.e. competition between H^+ ions and metal cations is observed. At pH 2-4, H^+ ions and metal cations still completely fill the functional groups, but the latter begin to be deprotonated. At pH 7, the carboxylic acid residue of the functional group is deprotonated, and at pH 12 the iminodiacetate group is completely deprotonated (figure 3).

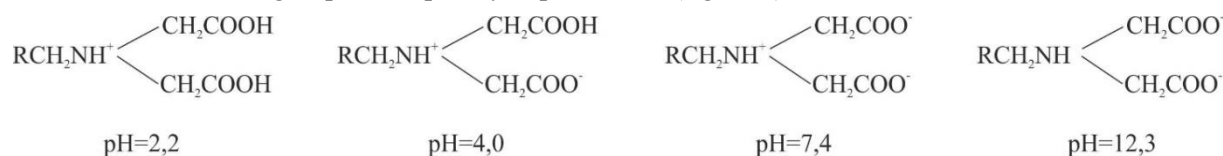


Figure 3. Influence of pH on iminodiacetate functional groups.

Although the latter case is more favorable for the sorption of cations due to the absence of hydrogen ions in the functional groups, maximum of metal cations sorption occurs at a pH value about 5.

To study the effect of pH on the sorption of nickel (II), model solutions of nickel with different pH were prepared. Samples of ion exchanger weighing 1 g in H^+ -form were brought into contact with the solution. Duration of sorption was 24 hours; the results are shown in figure 4.

Obtained data shows that ion-exchange resin Lewatit TP207 has the maximum capacity for Ni (II) at pH=4-4.5. Thus, during the leaching operation, obtaining of solutions with a pH close to this value is preferable or the pH of the leachate should be adjusted.

Sorption of nickel from leach solution was carried out in a column with a diameter of 1 cm and a length of 50 cm. Lewatit TP-207 (25 cm³) was loaded into the sorption column. The solution was passed through a sorption column at a constant rate of 4 specific volumes per hour and 25 cm³ samples were taken.

During nickel sorption in the column, competitive sorption of calcium ions was detected. The concentration of calcium ions in the leach solution is comparable to the concentration of nickel ions. When the solution was passed through the column, nickel was first sorbed, the ion exchanger turned blue. The colored front moved along the height of the column. Further nickel displacement was observed. Analysis of the filtrates showed the absence of calcium ions in them. With an increase in the total length of the ion exchanger layer by a factor of 10, displacement of sorbed calcium ions and repeated sorption of nickel ions were observed. A similar sorption behavior of calcium is described in [20].

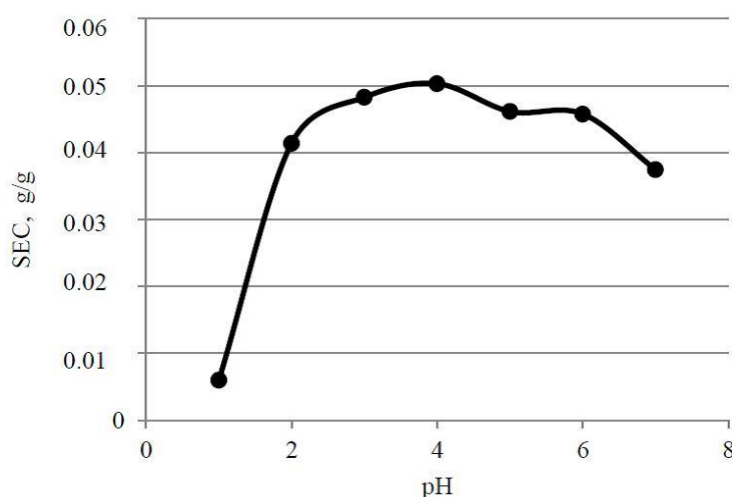


Figure 4. Dependence of SEC for from pH value.

3. Conclusions

Thus, for the processing of nickel-chromium galvanic sludges hydrometallurgical technology can be used. The proposed scheme includes steps of sludge leaching with sulfuric acid solutions, pH correction and selective sorption of nickel by synthetic ion-exchange resin Lewatit TP207. Competitive sorption of calcium ions inhibiting the sorption of nickel ions was detected. To reduce this effect, it is recommended to increase the total height of the ion exchanger layer.

References

- [1] Twidwell L G and Dahnke D R 2001 Treatment of metal finishing sludge for detoxification and metal value *The European Journal of Mineral Processing and Environmental Protection* **1(2)** 76–88
- [2] Ødegaard H, Paulsrud B and Karlsson I 2002 Wastewater sludge as a resource: Sludge disposal strategies and corresponding treatment technologies aimed at sustainable handling of wastewater sludge *Water Science & Technology* **46(10)** 295–303
- [3] Pérez-Villarejo L, Martínez-Martínez S, Carrasco-Hurtado B et al 2015 Valorization and inertization of galvanic sludge waste in clay bricks *Applied Clay Science* **105–106** 89–99
- [4] Stanisavljevic M, Krstic I and Zec S 2010 Eco-technological process of glass-ceramic production from galvanic sludge and aluminium slag *Science of Sintering* **42(1)** 125–130

- [5] Ozdemir O D, Figen A K and Piskin S 2011 Utilization of galvanic sludge as raw material for production of glass *Proc. of the Int. Conf. on Chemistry and Chemical Process* **10** 45–49
- [6] Bocanegra J J C, Mora E E and González G I C 2019 Galvanic sludges: Effectiveness of red clay ceramics in the retention of heavy metals and effects on their technical properties *Environmental Technology & Innovation* **16** 100459
- [7] Orescanin V, Mikulic N, Mikelic I L, Posedi M, Kampic S and Medunic G 2009 The bulk composition and leaching properties of electroplating sludge prior/following the solidification/stabilization by calcium oxide *Journal of Environmental Science and Health A* **44** 1–7
- [8] Stepanov S, Morozov N and Morozova N 2016 Efficiency of use of galvanic sludge in cement systems *Procedia Engineering* **165** 1112–1117
- [9] Bednarik V, Vondruska M and Koutny M 2005 Stabilization/solidification of galvanic sludges by asphalt emulsions *Journal of Hazardous Materials* **122(1–2)** 139–145
- [10] Arsenovic M, Radojevic Z and Stankovic S 2012 Removal of toxic metals from industrial sludge by fixing in brick structure *Construction and Building Materials* **37** 7–14
- [11] Andreola F, Barbieri L, Bondioli F, Cannio M, Ferrari A M and Lancellotti I 2008 Synthesis of chromium containing pigments from chromium galvanic sludges *Journal of Hazardous Materials* **156** 466–471
- [12] Olshanskaya L, Danilova E and Lazareva E 2018 Extraction of Nickel Hydroxide from Galvanic Waste Production for the Manufacture of the Nickel-Cadmium (Iron) Battery *Ecology and Industry of Russia* **22(6)** 4–9
- [13] Świerk K, Bielicka A, Bojanowska I and Maćkiewicz Z 2007 Investigation of Heavy Metals Leaching from Industrial Wastewater Sludge *Polish J. of Environ. Stud.* **16(3)** 447–451
- [14] Tokach Y E, Rubanov Y K, Pivovarov N A and Balyatinskaya L N 2013 Galvanic Sludge Recycling with the Extraction of Valuable Components *Middle-East J. Sci. Res.* **18(11)** 1646–1655
- [15] Silva J E, Paiva A P, Soares D, Labrincha A and Castro F 2005 Solvent extraction applied to the recovery of heavy metals from galvanic sludge *Journal of Hazardous Materials* **B120** 113–118
- [16] Shi T, Zou S, Liu J, Zuo L and Lv C 2011 Separation and Recovery of Nickel and Copper from Multi-Metal Electroplating Sludge by Co-Extracting and Selective Stripping *J Civil Environment Eng* **1(1)**
- [17] Evaristo A A A, Santos K C R, Costa L C and da Marques M R 2013 Evaluation of ion exchange resins for recovery of metals from electroplating sludge *Polymer Bulletin* **70(8)** 2239–2255
- [18] Makovskaya O Yu, Kostromin K S 2019 Leaching of non-ferrous metals from galvanic sludges *Materials Science Forum* **946** 591–595
- [19] Silva J E, Soares D, Paiva A P et al 2005 Leaching behaviour of a galvanic sludge in sulphuric acid and ammoniacal media *Journal of Hazardous Materials* **B 121** 195–202
- [20] Timofeev K L, Naboychenko S S, Lebed A B and Akulich L F 2013 Kinetics of zinc, calcium and magnesium sorption from water solutions, using the aminodiacetic ionite Lewatit TP-207 *Non-ferrous metals* **8** 59–64